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REPLACEMENT CARBON FIBERS FOR THERMAL PROTECTION APPLICATIONS.(U)

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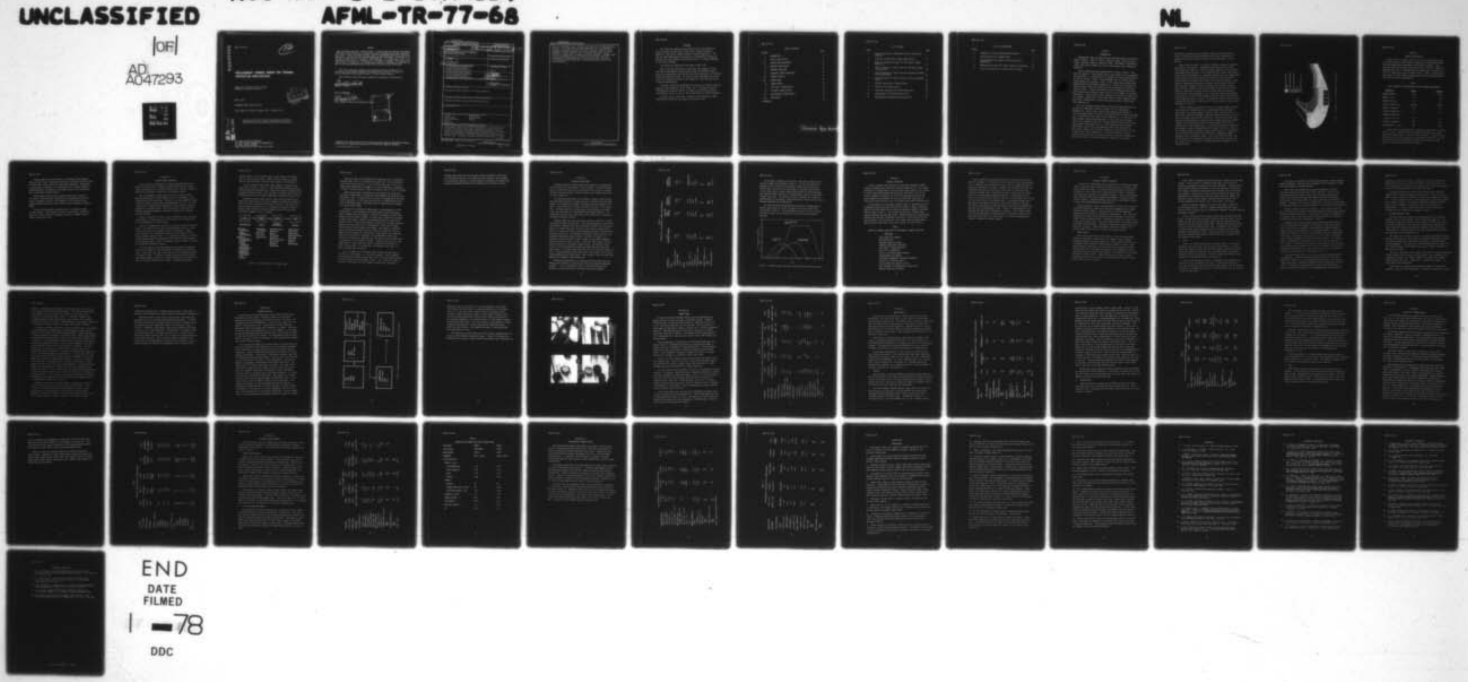

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REPLACEMENT CARBON FIBERS FOR THERMAL PROTECTION APPLICATIONS

Composite & Fibrous Materials Branch
Nonmetallic Materials Division

August 1977

TECHNICAL REPORT AFML-TR-77-68

Final Report for Period 1 January 1977 - 26 April 1977

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AIR FORCE MATERIALS LABORATORY
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Donald L. Schmidt

DONALD L. SCHMIDT

FOR THE COMMANDER

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Chief, Composite and Fibrous Materials Branch

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Fibrous carbons are low cost engineering materials. They are used in a large number of specialty aerospace and industrial applications because of their flexibility, high thermal stability, light weight, chemical inertness, low thermal conductivity, dimensional stability, low electrical resistivity, nontoxicity, nonflammability, and other attributes. Most grades of fibrous carbon are manufactured from the precursor continuous filament rayon. Because of declining commercial market for this textile

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product in the United States, continued availability is becoming more questionable. The evaluation of substitute materials, and, the development of equivalent replacement materials have been initiated to preclude future shortages or production delays. The area of greatest concern is the development of organic fabrics, which can later be converted to carbon fabrics for reinforcement of thermal protection composites. Fibrous organic precursors receiving the most attention are staple rayon, pitch and polyacrylonitrile (PAN) materials. This report describes the status of candidate precursor fibers and the carbonized products derived from these materials.

FOREWORD

This report was prepared by the Composite and Fibrous Materials Branch, and was initiated under Project 2417, "Thermal Protection Materials", Task 241701, "Reentry Vehicle Protective Materials". The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. D. Schmidt (AFML/MBC) as the Project Engineer.

This report was submitted by the author in April 1977.

Some of the items described in this report were commercial items that were not developed or manufactured to meet any Government specification, to withstand the tests to which they were subjected, or to function as applied during this study. Any failure to meet the objectives of this study is no reflection upon any of the commercial items discussed herein or upon any manufacturer.

The author gratefully acknowledges the assistance of several technical experts in the preparation of this report. Mr. S. Schulman of the Air Force Materials Laboratory and Mr. G. Shepard of the HITCO Corporation provided data, and Dr. B. Butler, Sandia Laboratories provided photographs.

A portion of this report was presented at the 22nd National SAMPE Symposium and Exhibition, San Diego, CA, 26-28 April 1977.

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SECTION I

INTRODUCTION

Carbonaceous fibers are among the most promising engineering materials known to mankind. They are flexible, thermally stable, light-in-weight, strong, infusible, nontoxic, chemically inert, nonflammable, dimensionally stable, electrically conductive, low cost, and possess other interesting properties.

Fibrous carbons have been manufactured for almost a century. They were first used by T. Edison about 1879 as the filament in his incandescent lamp (Reference 1). The technology laid dormant for many succeeding years, but then in the early 1950's, various nonwoven forms of fibrous carbons became commercially available. Later in 1959, woven carbon products were manufactured by batch methods (Reference 2). Carbon felts and batts were commercialized in 1960, and, carbon yarns were produced by a continuous process in 1961. In 1965, high modulus and high strength graphite yarns were manufactured by applying tensile strain to the filaments at elevated temperatures. Today, fibrous carbon products are available as staple fiber or continuous filament yarns, tows, woven fabrics, tapes, nonwoven sheets, mats, batts, needled felts, and woven multidirectionally reinforced preforms (Reference 3).

The first continuous carbon fibers were manufactured industrially by pyrolysis of regenerated cellulose (rayon) in an inert atmosphere (Reference 4). These fibrous carbons found numerous applications in ultra-high temperatures, but their low strength and elastic moduli precluded use in structural and other applications (Reference 5). In the search for other suitable carbon-forming precursors, it was found that pyrolyzed fibers with interesting properties could be obtained from polyacrylonitrile (PAN) polymers (References 6 and 7). These fibers had high stiffness, high modulus, high density, and moderately high thermal conductivity. Such fibers, however, were relatively expensive or available only in high filament count, large diameter tows. Continued exploration of other polymeric precursors lead to pitch-based fibrous precursors (Reference 8). These latter materials yielded inexpensive, moderately low strength,

high modulus, high density, and thermally conductive pyrolyzed fibers. Fibrous carbons have thus been developed with various combinations of properties and physical forms to meet the specialized needs of varied markets.

Carbon fibers are used in a variety of defense, aerospace, industrial, and scientific applications. Important defense applications include: high temperature insulation, reinforced carbon/carbons for aircraft brakes, radioisotope power containers, solid propellant motor nozzles, and reentry missile nosetips (Reference 9). Important aerospace uses are: leading edges of space shuttle vehicles, primary and secondary aircraft structures, turbine engines, helicopter rotor brakes, and similar applications. Some important nonaerospace applications include: sporting goods like golf clubs and tennis rackets, industrial equipment for corrosion resistant tanks, bearings, automobile leaf springs, medical prosthetic devices and implants, pump packing, and other uses like high speed, reciprocating, oscillating or rotating machinery. One of the most technically demanding of defense uses is for ablative thermal shielding of reentry vehicles and rocket propellant motors. Figure 1 illustrates the uses of fibrous carbons for ablative and insulative protection of a solid propellant rocket nozzle (References 10 and 11).

Fibrous carbons are being used in an ever increasing number of applications because of decreasing costs, increasing performance features, availability in a greater number of physical forms, and availability of design data. Materials produced to date have exhibited long service lives, ease of manufacturing, and high reliability. Fiber costs have been low, ranging from about $18.00 per pound for high strength carbon yarn (160,000 filament tow) to $320.00 per pound for high strength, high stiffness graphite yarn (1,000 filament tow). In general, performance has been more than adequate, often with higher density, strength, stability, stiffness, and fracture toughness compared to other fibrous materials. The materials can be procured from several different sources, although the number is decreasing due to economical reasons. Most of the fibers and their composites are well characterized with respect to properties, service life, etc. which in turn is leading to improved designers confidence for use in new applications.

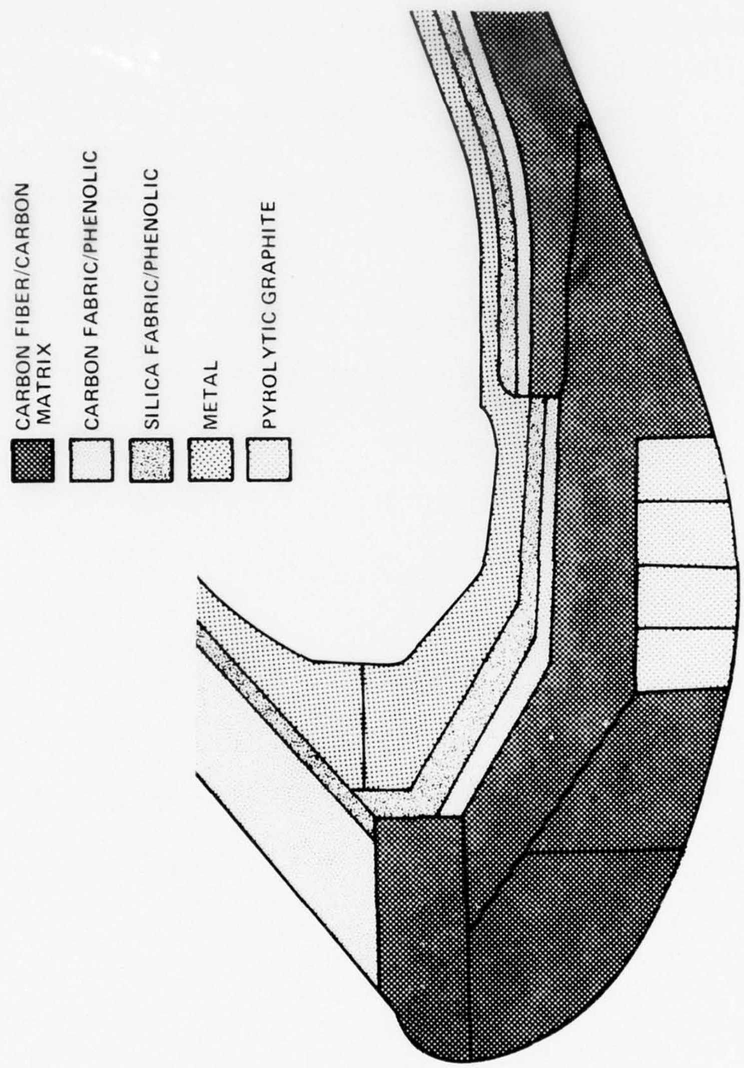

Figure 1. Schematic of a Solid Propellant Rocket Nozzle

SECTION II

FIBER CLASSIFICATION

Carbon fiber is a general term to cover all pyrolyzed fibrous materials which have been heat treated to temperatures substantially higher than the decomposition temperature of the precursor polymer. These pyrolyzed fibers are further classified as either "carbon" or "graphite," depending upon their (a) maximum processing temperature, (b) degree (or lack) of crystallinity, and (c) carbon content. Table 1 contains typical properties of fibrous carbons and graphites which have been manufactured from rayon precursors (Reference 12).

TABLE 1

TYPICAL PROPERTIES OF RAYON-BASED FIBROUS CARBONS AND GRAPHITES

PROPERTIES	CARBON	GRAPHITE
CARBON CONTENT, %	90.0	98.8
DENSITY, gm/cc	1.53	1.32
DIAMETER, microns	9.5	8.9
TENSILE STRENGTH, psi	120,000	90,000
TENACITY, gm/denier	6.2	5.3
ULTIMATE ELONGATION, %	2.0	1.5
THERMAL CONDUCTIVITY, Btu/hr/sq ft/°F/ft	13	22
STIFFNESS, gm/denier	310	350
SURFACE AREA, sq. m/gm	130.	1 to 4

Carbon fibers are manufactured at temperatures above 800°C, typically 1000° to 1400°C. Graphite fibers are prepared at substantially higher temperatures (above 2000°C), typically 2400° to 2600°C. Partially carbonized fibers have also been prepared at temperatures below 800°C, but they are not used in ultra-high temperature applications because of their thermal instability and high volatile content.

Fibrous carbons are relatively easy to distinguish from graphite fibers by their lack of crystalline orientation (disordered microstructure). In other words, carbon fibers are always highly amorphous. Some degree of crystallinity is present in all pyrolyzed fibers, however, because of retained molecular orientation, crosslinked structure, and orientations due to spinning and stretch strains.

Carbon fibers typically have a higher surface area, electrical resistivity, moisture content, wettability by conventional liquids and resins, elongation at break, fiber diameter or cross-sectional area, thermal expansion coefficient, and volatile content compared to graphite fibers.

The most distinguishable characteristics of the graphite fibers include a higher: carbon content, degree of crystallinity, thermal conductivity, purity, oxidative resistance, lubricity, strength, elastic modulus, and specific heat.

SECTION III

FIBROUS RAYON PRECURSORS

Fibrous carbons and graphites are largely manufactured from the precursor viscose rayon. Continuous filament rayon has been the most widely used because of its suitable carbon content, low cost, commercial availability, and ease of conversion to carbonized products.

The first commercial rayon plant was built in France in 1891. Research performed by a French chemist, Count H. de Chardonnet led to industrialization of the process. Because of the great demand for rayon in women's apparel, fibrous rayon was manufactured in the U.S. in 1910. In the 1930's, filaments were produced with finer diameters, improved strengths, and uniform quality. By the late 1930's, high tenacity or stronger yarns were produced by controlled stretching with improved spinning equipment.

Rayon is available as viscose rayon, cuprammonium rayon, and saponified acetate. Of these materials, viscose rayon is most widely used for the manufacture of fibrous carbons.

Rayon is a thermosetting polymer which contains cyclized cellulosic chains. The fibers contain crystalline and amorphous domains, as well as microfibrils having a diameter of about 250 angstroms. Rayon is often referred to as "regenerated cellulose" to distinguish it from purely synthetic chemical fibers. It is chemically composed of cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxyl groups. Rayon is composed of about 44 weight % of carbon and a substantial amount of oxygen.

The four types of rayon fiber produced from viscose are regular tenacity, high tenacity, high wet modulus, and high wet strength materials. These fibers are used in end items alone or blended with natural or synthetic fibers. A variety of industrial and textile applications have been developed, with most of current production going to commercial uses. Some major industrial uses include: disposable and durable

nonwoven fabrics, tires, belting, hoses, sewing thread, and cordage. Textile fiber end uses include: apparel linings, draperies, apparel fabrics, home furnishings, braiding, narrow fabrics, and other uses.

The basic materials and process steps employed in manufacturing rayon fiber are shown in Figure 2. Both continuous and batch spinning processes have been developed, with single line capacities between 40,000 and 60,000 pounds per month. Both continuous and staple rayon fibers are produced, but most of the current production is devoted to staple fiber.

Continuous filament rayon used for carbon yarns and fabrics has a density of 0.0542 lb/cu inch, tensile strength of 65,000 psi, diameter of 0.0016 inch, and a surface area of about 0.5 sq m/gm. The fibers also have a maximum ash content of 0.7%, a maximum zinc content of 0.07%, a maximum sulfur content of 0.25%, pH between 5.0 and 8.0, and finish extractables between 0.2 and 1.0 weight %.

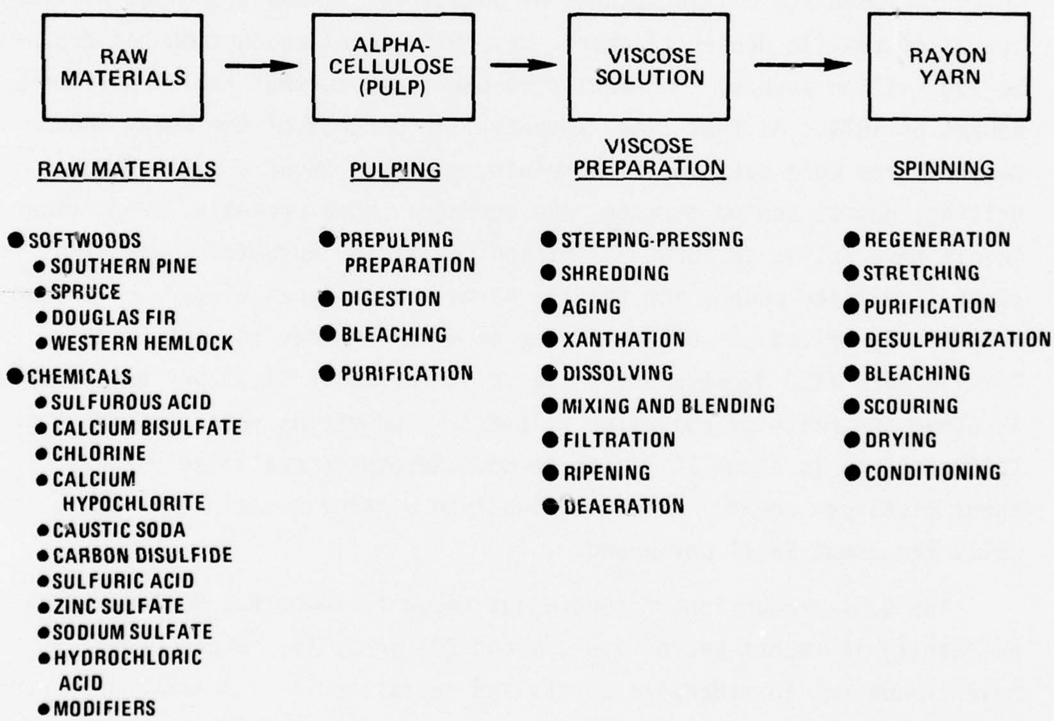

Figure 2. Process Outline for Filament Rayon

Rayon yarn used in the manufacture of carbon textiles is supplied on packaged tubes, with 8 to 10 pounds of yarn per tube. Typical specification values for the yarn are: 1.6 to 2.4 twists per inch, 10.3 to 13.5 pounds conditioned tensile strength, 5.5 to 9.5% elongation, a maximum of 13 weight % moisture content, 1590 to 1710 denier, and 2.9 to 4.7% shrinkage.

Rayon yarn has been a relatively low cost material for many years. Continuous filament yarn in 1100 denier, 480 filament sold for about $0.78 per pound in 1971. In January 1972, the price of 1100/480 denier yarn rose to $1.13 per pound. At the same time, the price of 1650/720 denier yarn sold for $0.98 per pound. The present price of 1650/720 yarn is between $1.63 and $1.80 per pound.

Production of continuous filament rayon is being phased out in the United States. Total production in 1968 was about 350 million pounds, which included 200 million pounds of industrial filament and 150 million pounds of textile denier filament. By 1970, total production had dropped to 230 million pounds. Manufacturing decreased further to 154 million pounds by 1974. At that time, seventy-five percent of the heavy industrial denier yarns were used for tire reinforcements. Other uses included belting, hoses, sewing threads, and cordage. More recently, production levels have fallen to about 78 million pounds for industrial yarn and about 15 million pounds for textile yarns. Both types of yarn have been essentially priced out of the market on a performance-to-cost basis. Textile yarn (150 denier) presently sells for about $1.25 per pound, which is above the price of polyester filament. Industrial yarn for tire cord (2200 denier) is about $0.72 per pound. Aerospace qualified yarn is about $1.63 per pound. After weaving into 8-harness satin fabric, it sells for about $3.61 per pound.

The U.S. production of continuous rayon filament has declined significantly in recent years, i.e., about 20% annually. Rayon producers have chosen not to modernize plants and install pollution controls because of severe competition from synthetic fibers. It is within the realm of possibility that there will be no domestic production of continuous

filament rayon within the next few years unless the demand is stabilized and profitability assured. The relatively small volume of rayon required by the aerospace industry for fibrous carbons and graphites is insufficient to ensure continued profitability and retention of the source of supply.

SECTION IV

AEROSPACE RAYON NEEDS

Aerospace qualified fibrous carbons and graphites are manufactured from a special processed industrial rayon filament. Over 200 different types of industrial and specialty rayon yarns were originally evaluated to obtain the best balance of rayon-to-carbon yield, handling qualities, and fiber properties.

The aerospace requirements for continuous filament rayon have been satisfied almost entirely by single ply yarn. Production has been about equally split between 720 filament, 1650 denier and 480 filament, 1100 denier. Most of the yarn is woven into fabric and used in this textile form. The 1650 denier yarn has been woven into 8-harness, satin woven cloth, and used primarily to manufacture carbonaceous products. The 1100-denier yarn has been largely woven into a plain fabric, and used to manufacture graphitic products.

Aerospace needs for rayon yarns were originally satisfied in 1964 by the Industrial Rayon Company (IRC). They ceased production of their aerospace grade in December 1972 due to decreased profitability, diminishing supply of suitable wood pulp, scarcity of pure caustic, higher profitability of staple rayon fiber, and environmental problems associated with antiquated facilities. A replacement continuous filament rayon was subsequently developed by American Enka, a subsidiary of Akzona, Inc. Evaluation and qualification of their product by the defense community amounted to many millions of dollars. About May 1975, American Enka Co. ceased production of continuous filament rayon. The American Viscose Division of the Food Machinery Corporation (FMC) then qualified their rayon product. In October 1975, the Fiber Division of FMC was offered for sale. A new organization (AVTEX Fibers, Inc.) was formed in July 1976 to continue manufacturing these fibers. Their product is the sole remaining, domestically produced, qualified material.

Although the manufacturers of aerospace qualified rayon yarn have changed, the properties of the yarn and fabric have remained remarkedly constant. This is illustrated in Table 2, which contains selected properties of yarns and fabrics from three successive producers.

TABLE 2

EVOLUTION OF CONTINUOUS FILAMENT RAYON FABRICS

PROPERTIES	IRC-AMERICAN CYANAMID	AMERICAN ENKA COMPANY	AMERICAN VISCOSE-FMC	AMERICAN VISCOSE-FMC
YARN				
DENIER, gm/9,000 m	1,659	1,591	1,616	1,100
FILAMENT/YARN	720	720	720	480
PLIES	1	1	1	1
FABRIC				
STYLE	8-HS	8-HS	8-HS	SQUARE WEAVE
WEIGHT, oz/sq yd	16.13	15.12	16.20	17.4
WIDTH, in	49.0	49.0	49.1	60.0
THICKNESS, in	0.0280	0.0255	0.0290	0.033
THREAD COUNT, yarns/in				
WARP	37	35	37	20
FILL	37	35	37	17
BREAK STRENGTH, lb/in				
WARP	380	304	420	550
FILL	374	293	434	525
MOISTURE CONTENT, %	10.7	10.3	9.90	8 to 10

The aerospace community utilizes only a very small fraction of continuous filament rayon produced in the U.S. In 1972, one fiber plant produced 60 million pounds of continuous filament rayon yarn for non-defense needs, and only two million pounds for aerospace requirements. In more recent years, fibrous carbons and graphites for aerospace needs have required between 625,000 to 1,750,000 pounds annually of continuous filament rayon yarn. This amount of material converts into 125,000 to 350,000 pounds of low modulus, carbon and graphite fibers, which are worth between $5,000,000 and $14,000,000.00.

The total and annual projected continuous rayon filament needs for ablative applications of several aerospace and military systems are illustrated in Figure 3. The requirements are highly cyclic, vary with the type of system, and are difficult to forecast with any degree of certainty.

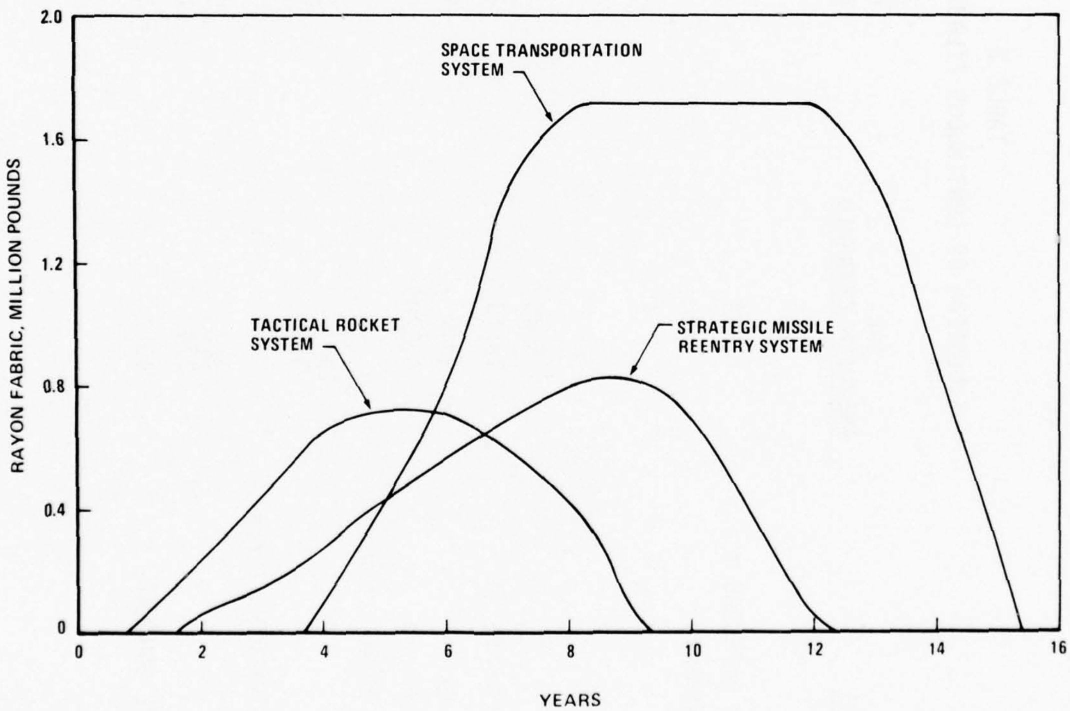

Figure 3. Projected Rayon Yarn Needs for Several Aerospace Applications

SECTION V

SHORTAGE INDICATORS

Critical aerospace applications utilizing high performance fibrous carbons and graphites may experience future shortages due to: (a) limited availability or nonavailability of the fibrous rayon precursor; (b) limited or lack of specialized manufacturing pyrolysis facilities; (c) loss of existing commercial producers; (d) artificial shortages created by temporary commercial over-demand; (e) slow or ineffective resolution of priorities by existing users; and (f) possibly other factors (Reference 13).

The availability of continuous filament rayon for aerospace qualified carbonaceous products has been difficult to forecast. Several indicators, however, have been identified for evaluating potential materials shortages. They are shown in Table 3. With respect to continuous filament rayon, numerous problem areas have been noted. Delayed production or discontinued manufacturing have been likelihoods, especially in view of declining commercial markets, low profitability, cyclic needs, more stringent government production regulations, high cost of energy, and other factors.

TABLE 3

MATERIALS SHORTAGE INDICATORS FOR CONTINUOUS FILAMENT RAYON YARN

INDICATORS
SINGLE QUALIFIED PRODUCER
LOW PROFITABILITY
UNCERTAIN PRODUCTION NEEDS
INCREASED REGULATORY CONSTRAINTS
HIGH ENERGY TO PRODUCTION RATIO
HIGHLY CYCLIC PRODUCTION
FEW SUBSTITUTE/REPLACEMENT MATERIALS
LIMITED NONMILITARY MARKET
NO MATERIALS MANAGEMENT INFORMATION PROGRAM
LOW LEVEL OF TECHNICAL GROWTH
LIMITED PRODUCTION CAPACITY CAPITAL
RAPID INCREASE IN RAW MATERIALS & LABOR COSTS
OBSOLETE PRODUCTION EQUIPMENT

Various approaches have been developed for alleviating or minimizing materials shortages. Profitability can be increased by subsidizing product prices. Material can be stockpiled for the life of a system provided firm production requirements are known. Purchase from foreign sources has sometimes been possible, but usually not in the case of a relatively pure, continuous filament rayon. Specification can be relaxed, but that would result in an unacceptable performance reduction. The defense priority system can be used to divert material from the civilian sector, but civilian uses for carbon fabrics are presently small. A government owned plant is yet another, but expensive option for alleviating a materials shortage. The use of a replacement or substitute material can often be employed with some sacrifice in performance or cost. Finally, alternate materials can sometimes be identified or developed if necessary. Of all these options, only the alternate material approach results in minimum influence on the free enterprise system. For that reason, it is often the preferred approach to a materials shortage problem.

SECTION VI

ALTERNATE FIBROUS PRECURSORS

In view of the questionable future availability of continuous filament rayon, a search has been initiated to evaluate, develop, and qualify other types of precursor fibers. The leading alternate precursors identified to date are: staple rayon fiber, polyacrylonitrile (PAN) in continuous and staple forms, and pitch in continuous filaments. Other less promising fibers have been derived from condensation polymers, including polyvinyl alcohol, phenolics, polybenzimidazole, polyacetylene, polyimides, furfuryl alcohol, and tetrabenzophenazine (Reference 14).

Fibrous precursors used in the manufacture of carbon fibers should be relatively inexpensive, commercially available, homogeneous, and carbon-containing textile products. They should have a melting temperature substantially higher than its decomposition temperature. The virgin fiber should possess a high carbon content and retain a maximum of the carbon content in the pyrolyzed residue. Contaminants should be a minimum in the virgin and pyrolyzed fibers. Pyrolysis should proceed in an orderly fashion and without large exotherms. Appreciable liberation of carbon-containing gases must not occur. Energy requirements should be a minimum. The fibrous product should also be a strong, yet flexible material.

1. STAPLE RAYON

While staple rayon fibers do not offer all of the high performance features of continuous filament rayon, they appear to be an adequate replacement material for many applications. Their primary attributes are: a reasonably stable commercial market, multiple domestic sources, lower (about one-half) fiber costs, versatility for yarn constructions, demonstrated carbon fiber technology, and characteristics somewhat similar to the baseline precursor and finished products. Some staple fiber limitations encountered to date include: lower strength yarn and fabric, greater thickness yarn and fabric, and additional manufacturing steps to card the staple fibers and ply into yarns.

Staple fiber is prepared by cutting continuous filaments to prescribed lengths. Fiber spinning is the same for both types, but significant economical advantages are achieved with staple materials. Large, multiple-hole (25,000 to 40,000) spinnerettes can be used, compared to the typical 720 filament spinnerettes used to make small diameter yarns for the aerospace industry. Additional savings are often achieved with staple fiber manufacturing, including high volume continuous production, cheaper raw materials, higher spinning speeds, spinning baths optimized for fast solvent evaporation and recovery, sale of by-products, and others.

Domestic production capacity for staple rayon fiber is about 725 million pounds annually. Four U.S. companies manufacture this type of material, which is used primarily in disposable nonwovens, household textiles, and apparel textiles.

Prior to 1973, the price of regular staple rayon was under \$0.30 per pound. By late 1973, the price had increased to \$0.33 per pound. By the spring of 1974, the price of regular rayon staple had reached \$0.58 per pound and \$0.63 for high-wet modulus fiber. Regular rayon staple declined in price to \$0.50 per pound in early 1975. In September 1975, the price of regular rayon staple increased to \$0.54 per pound and to \$0.59 per pound for high-wet modulus fiber. Present rayon staple costs are about \$0.63 per pound, \$0.90 per pound for staple fiber yarn, and about \$2.90 per pound for woven fabric.

2. PITCH

Pitch is an attractive precursor for carbon fibers. It is readily available, very low in cost, and has a high carbon content. It can be formed into fibers with hot melt spinning equipment, and requires minimal electrical energy for conversion into a pyrolyzed product, and yields 95 weight % fiber upon pyrolysis. Production speeds are relatively high because of the low gas evolution during pyrolysis.

Pitch is derived from tar, which is obtained by the destructive distillation of coal, petroleum, peat, wood, or other organic materials. Coal tars are usually distilled to remove light chemicals, and the residue is known as a "treated tar" or pitch. Petroleum-based pitches are obtained in much the same manner.

Pitch fibers are produced from high molecular weight, highly oriented aromatic compounds. They are usually composed of 85 to 95 weight % carbon, with lesser amounts of hydrogen and ash.

Pitch fibers are manufactured by various techniques, including centrifugal spinning, blowing, and hot melt extrusion. The first two methods generally yield short fibers, while continuous filaments are typically obtained by extruding molten material through fine diameter spinnerettes. The as-spun fibers are usually about 10 to 20 microns in diameter. Because pitch fibers are thermoplastic, they must be crosslinked by oxidation to obtain an infusible material prior to pyrolysis (Reference 15).

Ordinary aromatic pitches are isotropic. Fibers produced from this type of material do not possess the preferred molecular orientation required for high strength and stiffness. Some degree of crystalline alignment can be induced in these fibers by tensioning during oxidation or significant stretching during pyrolysis (References 16 and 17).

Mesophase pitch fibers are manufactured from certain petroleum fractions or crudes which are composed of a two-phase, anisotropic liquid. Part of the liquid is composed of thermodynamically stable mesophase or liquid crystals and the remainder is an isotropic material. Fibers are formed by extruding hot pitch through spinnerettes and into a proprietary liquid bath. The resultant fibers consist of fine, rod-like elongated liquid crystals embedded in a relatively isotropic matrix. The isotropic matrix is subsequently rendered infusible by an oxidation treatment at 250° to 400°C. Preferred high orientation is obtained in the virgin fiber by the shear forces employed during spinning and drawing. Additional hot-stretching during pyrolysis is thus not necessary to obtain interesting properties in the carbon fibers (References 18 to 21).

Pitch-based carbon fibers of very high quality have been produced in the laboratory. Carefully filtered pitch was formed into fibers and pyrolyzed at 1700°C to 7.5 micron diameter carbon fibers. The resultant fibers had a tensile strength of 600,000 psi and an elongation at failure of 2.0%. Properties of production materials have been significantly poorer and variable to date due to the nonstandardized starting material

composition, volatiles, particles, contaminants, porosity, insufficient thermosetting of the pitch, and other factors. These difficulties are being corrected and the production of mesophase pitch fibers will approach several million pounds annually in the next five years.

Low modulus carbon fibers derived from pitch materials have been commercially available from Japan for several years. These fibers had typical tensile strengths of 150,000 psi and a tensile modulus of 7,000,000 psi. In 1973, a domestic source of high modulus pitch mat became available from a domestic company. This random oriented mat contained filaments having a tensile strength of 200,000 psi and a tensile modulus of 35,000,000 psi. In 1975, a woven carbon fabric, based on continuous filament pitch, was commercially introduced in the U.S.

3. POLYACRYLONITRILE (PAN)

PAN fibers have been found to be suitable precursors for graphite products, and to a lesser degree, various carbonaceous materials. The attributes of PAN fibers are high carbon content, low costs, availability in various filament count yarns and tows, stable market, demonstrated fiber formation technology, and multiple producers. Some of the current limitations are: limited availability in small diameter yarns and tows, and high alkali metal contaminant level.

PAN fibers are available in the U.S. from about three domestic sources and ten foreign sources. Fibers used in carbonaceous and graphite products are largely imported from Great Britain and Japan, and pyrolyzed under license agreements. Tow, staple yarn, and continuous yarns are used, but for economic reasons, large diameter tows such as 10,000 to 160,000 filaments are most common.

The cost of PAN fibers varies greatly with the form. PAN tow containing 10,000 filaments sells for about \$3.50 per pound. Yarn containing 1,000 filaments or tow split to a similar number of filaments costs between \$7.00 and \$10.00 per pound. Staple yarn is significantly cheaper, i.e., about \$0.80 to \$2.50 per pound.

PAN fibers are produced from high molecular weight, linear organic compounds. They are either homopolymers, copolymers, terpolymers, or graft

polymers. Copolymeric and terpolymeric fibers have been found to be the most suitable for producing fibrous carbons. Their chemical compositions vary somewhat, but in all cases, they contain not less than 85 mol % acrylonitrile and not more than 15 mol % of a monovinyl compound such as methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidine chloride, or the like. A representative fiber chemical composition is 68 weight % carbon, 26 weight % nitrogen, and 6 weight % hydrogen.

Continuous and staple PAN fibers are spun by either a wet or dry process. In the wet process, the PAN polymer is batch produced, blended, and dissolved in a hot solvent like dimethylformamide (DMF) or sodium thiocyanate. The polymer solution is degassed, filtered, and then extruded under pressure through spinnerettes having from 1,000 to 12,000 holes and a diameter from 2 to 20 mils. The spinnerettes are immersed in a coagulation bath which is typically 85% DMF and 15% water. Fiber formation commenses at the face of the spinnerette by the action of the nonsolvent in the bath. The newly formed fiber is essentially a swollen gel consisting of a mixture of polymer, solvent, and nonsolvent. Volumetric and longitudinal contractions occur as the fiber progresses through the bath. The nonsolvent diffuses inward and the solvent diffuses outward with the formation of voids, which depend upon the specific coagulation conditions. The fiber is stretched up to four times in a preheated bath, stretched 6 to 24 times in steam, washed, finished, dried, and stored in high humidity. In the dry spinning process, the polymer-solvent solution is forced with a volumetric pump through an array of orifices (spinnerettes) into a vertically aligned column or stack to remove the solvent as the fiber line falls to a collecting or winding apparatus. As the solvent (such as dimethylformamide) vaporizes, the fiber skin collapses and the cross section assumes a general shape of a rounded dumbbell (References 22 to 24).

Molecular orientation of the PAN polymer is achieved by deformation in the spinning process and stretching during fiber formation. Fiber structure is stabilized by two hours pretreatment or oxidation under tension and in a high temperature (200° to 300°C) oxygen-containing atmosphere including air, ozone, or other oxidizing chemical agents in the form of gases, solutions, liquids or solids. This process treatment

produces an oriented cyclic or ladder structure which is sufficient to maintain preferred molecular orientation during carbonization (Reference 25).

PAN fibers contain a high level of alkali metals, which make them unsuitable for use in specialized heatshielding applications. A typical PAN fiber contains about 2,700 parts per million (ppm) of sodium, 50 ppm of potassium, 40 ppm of magnesium, 30 ppm of calcium, and a trace of lithium. In addition, other metallic impurities are added to the fibers in the form of a surface delustrant. The delustrant is titanium dioxide in varying amounts and in discrete particular form. The delustrant is difficult to remove from the fiber, and it lowers the strength properties of the carbonized fiber. Most of the alkali metals contained in the virgin fiber are retained during carbonization, thus pyrolysis is not an effective method for reducing the contaminant level of organic fibers.

SECTION VII

THERMAL PYROLYSIS

The pyrolysis of various precursor fibers results in significant differences in carbon yields. Cellulosic fibers like rayon have a molecular formula of $(C_6H_{10}O_5)n$ and contain 45 weight % of carbon. The carbonization yield of this material is very low, i.e., about 18 to 26 weight % of the original fiber. Polyacrylonitrile fibers have the approximate formula of $(C_3H_3N)n$ and a 68 weight % of carbon. The yield of fibrous carbon from this precursor is 30 to 52 weight %. Pitch fibers derived from petroleum feedstock have the virgin fiber molecular formula of (CH)n and a 95 weight % of carbon. The carbonization yield from this fiber is very high. From 87 to 90 weight % of the original fiber remains in the form of fibrous carbon.

The structure and properties of carbon fibers are controlled by the choice of raw material, heat treating cycle, use of chemical treatments during carbonization, and application of stress on the fibers during processing. Figure 4 illustrates the manufacturing process for fibrous carbons and graphites. The process is invariably a multiple step, batch, or combined batch and continuous method. The first step is to clean the yarn or fabric of any lubricant or surface contaminant. The fabric is washed in a detergent or appropriate liquid chemical and dried. The second step is to stabilize the organic structure. This step involves the removal of water from rayon fibers at 200° to 300°C for up to six hours, or oxidative conversion of thermoplastic fibers (like PAN or isotropic pitch) to thermosetting or crosslinked structures. The third step involves carbonization of the fibers. One approach is to loosely wind the fabric on an appropriate mandrel and then heat treat in a gas-fired furnace at 800° to 1400°C for one to four or more hours. Slow heating is preferred to minimize exotherms and vaporize the tars, hydrocarbons, carbon monoxide, and carbon dioxide in an orderly manner. The pyrolysis is carried out in a special atmosphere, such as an inert gas, acidic oxidizing gas or an alkaline reducing gas. The heat treated fabric is then optimally passed through an electric furnace at a higher

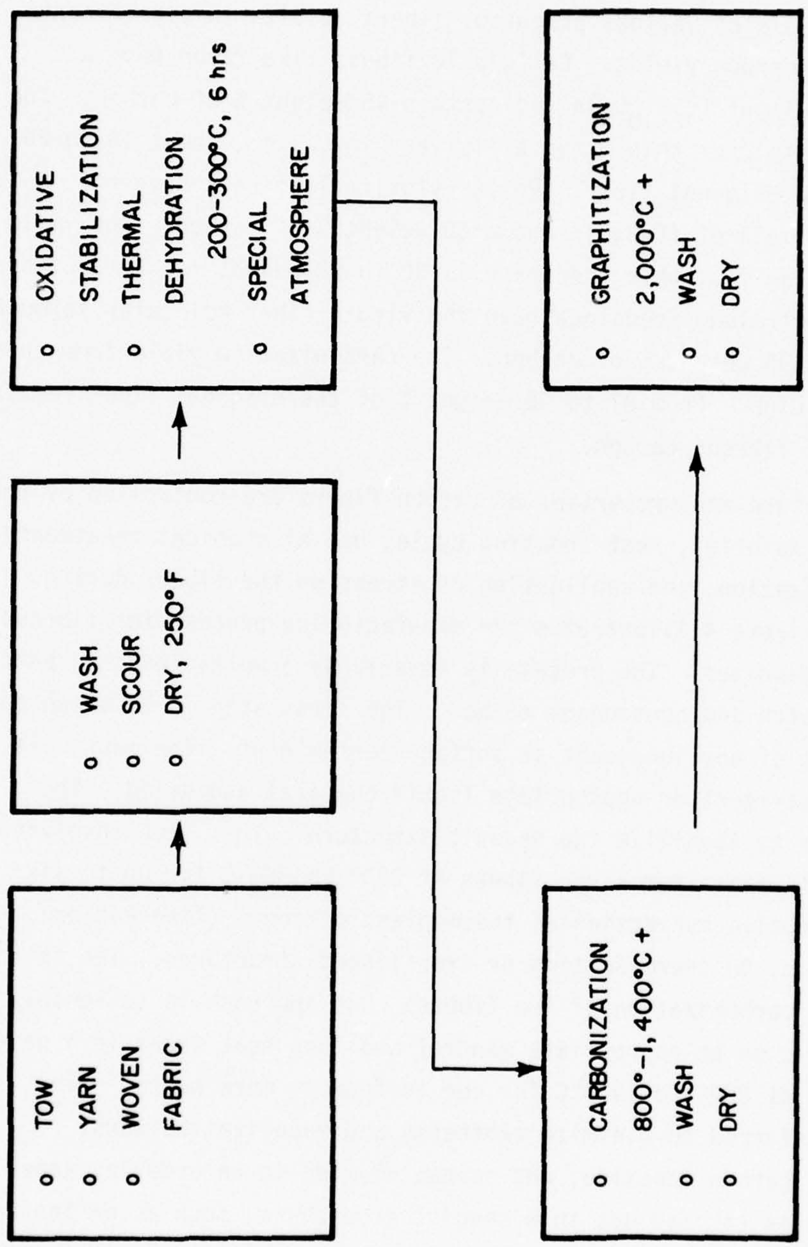

Figure 4. Manufacturing Process for Fibrous Carbons and Graphites

temperature and in the presence of an inert atmosphere like nitrogen. The resultant carbonized fabric is composed essentially of the element carbon, but it may also contain several percent of hydrogen, oxygen, nitrogen, halogen, phosphorus, boron, or other elements depending upon the virgin polymer composition, microstructure, mode of stabilization, and pyrolysis atmosphere. The carbonized fabric is then washed to remove residual particulate matter. If a more thermally stable graphitic product is desired, the material is further subjected to temperatures above 2000°C for about one hour. The graphitized product is then washed and dried (References 26 to 38).

The morphology of carbon fibers may differ greatly, depending upon the precursor and the thermal conversion process. Figure 5 illustrates the different cross sections of rayon, PAN and pitch-based fibers (Reference 39).

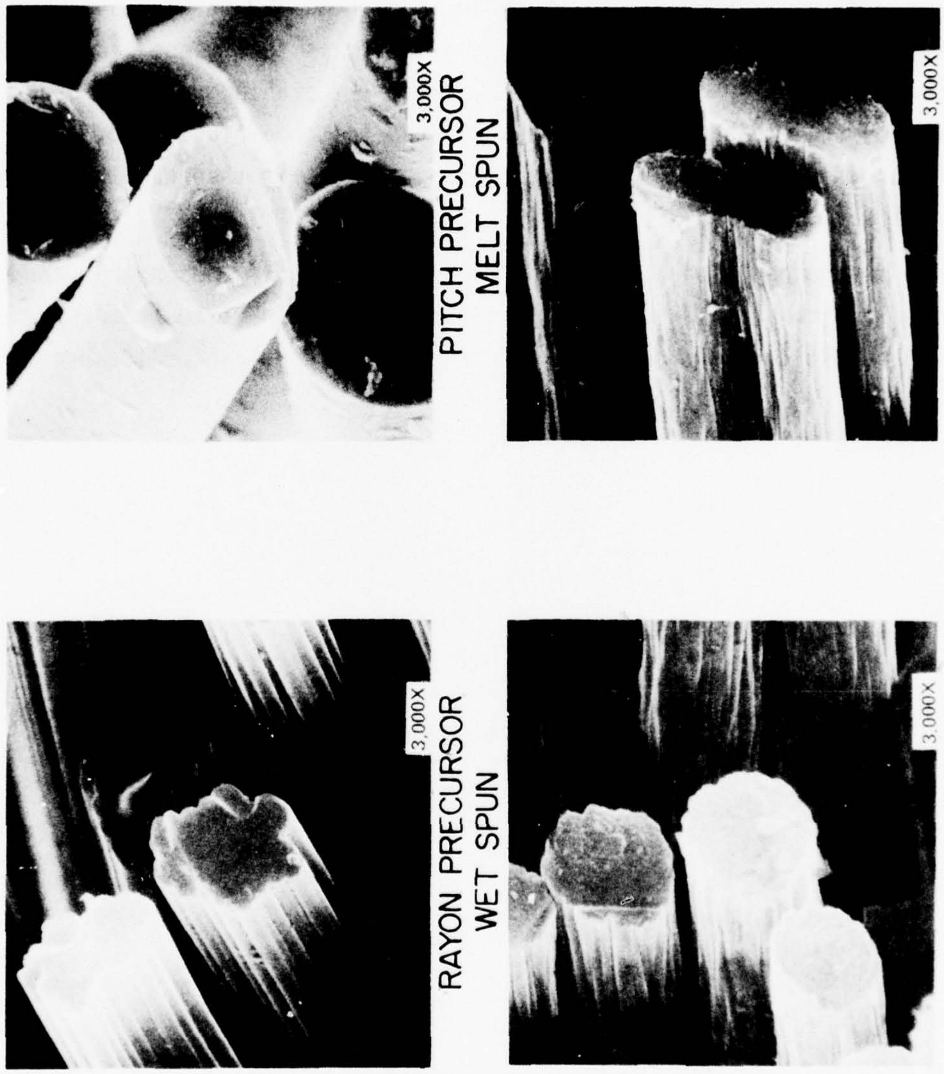

Figure 5. Typical Cross-Section of Various Carbon Filaments

SECTION VIII

CARBON YARNS

Continuous and staple filament carbon yarns are manufactured for sewing, weaving, knitting, braiding, and filament winding. Standard rayon-based yarn constructions are available in single and 2 plies, but 5-, 10-, and 20-ply materials are also available. Each ply contains a large number of individual filaments, typically 480 to 720 for rayon-based materials. PAN-based carbon yarns and tows are available in filament counts from about 384 to 160,000. Pitch-based yarns are manufactured in 720 filament material or near multiples thereof, with 2,000 filament yarn the most common.

Typical properties of rayon, PAN, and pitch-based carbon yarns are shown in Table 4. PAN-based carbon yarns are significantly higher in strength than the rayon-based or pitch-based materials. The pitch-based carbon yarns have a higher elastic modulus and density than the other fibers. Yarns composed of continuous filaments are higher in strength and smaller in diameter as compared to staple fiber yarns.

The price of high strength carbon yarns and tows varies greatly with the filament count. Typical prices are: $18.00/lb for 160,000 filament tow; $32.00/lb for 6,000 or 10,000 filament tows; $40.00/lb for 3,000 filament material; and $105.00/lb for 1,000 filament tow.

Low cost yarns are also available in the form of discontinuous filament (staple). For example, staple fiber PAN is prepared by breaking or cutting very large filament tows (160,000 filaments) into 0.5 to 4.0 inch lengths. Since this type of tow costs between $0.80 and $2.50 per pound, the resultant staple fiber yarn is correspondingly low in cost. The total staple fiber yarn process involves a series of sequential steps, including tow preparation, crimp removal, picker lap preparation, carding, drawing, roving, spinning, and ply twisting.

Most of the carbon yarns and tows used in aerospace structural applications are manufactured from PAN precursor. About 70,000 pounds per year of PAN-based fibrous carbons are used in aerospace and aircraft composites. Another 190,000 pounds per year are devoted to sporting goods, industrial applications, and prototype developments.

TABLE 4

TYPICAL PROPERTIES OF RAYON, PAN AND PITCH-BASED CARBON YARNS AND TOWS

PRECURSOR	RAYON	RAYON	PAN	PAN	PITCH
FIBER LENGTH	CONTINUOUS	CONTINUOUS	CONTINUOUS	STAPLE	CONTINUOUS
MANUFACTURER	UNION CARBIDE CORP.	HITCO	UNION CARBIDE CORP.	STACKPOLE	UNION CARBIDE CORP.
DESIGNATION	VYB 70 1/2	CY-2	WYP 30 1/0	PANEX 30/Y	VSA-11
FIBER PROPERTIES					
DENSITY, gm/cc	1.53	1.50	1.74	1.78	1.88
TENSILE STRENGTH, psi	120	140	361	225-300	175
TENSILE MODULUS, 10^6psi	6.0	6.0	33	30-38	50
CARBON CONTENT, %	90.0	94.0	92.0	-	96.9
YARN PROPERTIES					
PLIES/YARN	2	2	1	2	1
FILAMENTS/PLY	720	720	3,000	-	2,100
TWIST, turns/in	2.45	-	0.45	4.0	-
DIAMETER, in	0.030	.025	0.017	0.030	0.017
YIELD, yds/lb	3,100	3800	2,600	5200	11,000
DENIER, gm/9,000 m	1400	-	1,717	800	2,100
TENACITY, gm/den	3.8	-	-	-	-
BREAK STRENGTH, lb	7-9	2	13.5	-	-
ELECTRICAL RESISTANCE ohm/ft	185-210	152	-	-	-
COSTS, $/lb	66	-	86	38	20

SECTION IX

CARBON FABRICS

Carbon fabrics are manufactured in unidirectional, thin-to-thick bidirectional flat fabrics and tapes, circular and flat knitted goods, and multilayered constructions. The fabrics usually contain a single fiber type, but hybrid fabrics containing two or more types of carbon fiber have been prepared with unique properties. Standard fabrics are usually manufactured in 30- to 45-inch widths, and specialty materials have been woven in widths up to 80 inches. Fabric weights have varied from 1 to 32 ounces per square yard.

Carbon fabrics are manufactured by the pyrolysis of organic fiber cloths, or by weaving carbon yarns and tows. For rayon fibers, the preferred method of manufacture is to weave the cloth prior to the thermal treatment. Low modulus pitch-based and PAN-based yarns are typically oxidized, woven into fabric, and then converted to a carbon material.

The two major manufacturers of carbon fabrics are HITCO and the Union Carbide Corporation. Other organizations that either manufacture carbon fabrics or weave carbon yarns into fabrics include: Carborundum Company; Fabric Development, Inc.; Fabric Research Labs., Inc.; Fiberite Corp.; Hexcel Aerospace Co.; Polycarbon, Inc.; Minnesota Mining and Manufacturing; Prodesco, Inc.; Stackpole Fibers Co.; Textile Products Co.; and Woven Structures Div.-HITCO (Table 5).

1. WEAVING

Recent advances in weaving technology now permits uniform and high quality carbon fabrics to be woven from high tensile strength carbon yarns. The cost of weaving fabrics, of course, depends upon the volume. Typical weaving costs are on the order of $50.00 per pound for 50-pound lots and at little as $2.00 per pound for very large orders.

Very high strength, moderate modulus carbon fabrics are always prepared by weaving carbon yarns or tows on modified textile machinery. This approach avoids permanent fiber crimping and localized loss of strength properties during pyrolysis. The weaving of fabric is a multistep process. The small diameter yarn or tow is weighed, tested,

TABLE 5

TYPICAL PROPERTIES OF RAYON PRECURSOR CONTINUOUS FILAMENT 8-HS CARBON FABRICS

MANUFACTURER				
NAME	HITCO	UNION CARBIDE CORP.	CARBORUNDUM CO.	POLYCARBON, INC.
TRADE DESIGNATION	CCA-3	VCL	GSCC-8	CSA
CONSTRUCTION				
FILAMENT/YARN BUNDLE	720	720	720	720
PLIES/YARN	1	1	1	1
THREAD COUNT, yarns/in				
WARP	52	53	51	50-58
FILL	49	52	51	45-57
PROPERTIES				
WEIGHT, oz/sq yd	8.25	8.0	7.9	7-9
THICKNESS, in	0.018	0.02	0.018	0.019
WIDTH, in	35	43-45	30	32-43
CARBON CONTENT, %	95.5	97.0	99.0	94.0
ASH, %	0.20	0.75	0.5	0.5
pH	9.3	8.6	7.0	
BREAK STRENGTH, lb/in				
WARP	43	47	64	50
FILL	30	53	64	45
COSTS (APPROX) $/lb	$37.50	$37.50	$31.30	

and wound onto a larger diameter (about 3 inches) tube. The yarn is then taken from the winders and "creeled" in preparation for warping. Creeling is an operation whereby many small packages are mounted on a frame having spool or package mountings. Each individual yarn is withdrawn from each package under tension and in a programmed manner over and under yarn guides. Depending upon the fabric construction and end use, the yarn may or may not be treated with a protective sizing and/or lubrication compound. From the creel the yarn is passed through the sizing solution. Excess size is removed by passing the yarn through compression rolls and then dried. The yarn is then wound onto a reel where the warp for the loom is prepared. A sheet of parallel yarn is wound onto the warping reel at the same time. The end-product out of the slasher/warper is a series of parallel yarns wound onto a loom beam. Each of the parallel yarns on the loom beam is of sufficient length to weave the length of the desired fabric. The loom beam is then taken to a location where each of the yarns on the beam is drawn, one at a time, through heddle eyes which are part of the loom harnesses. The harnesses of the loom rise and fall in a programmed motion to form the weave of the fabric. Each of the yarns drawn through the harnesses is then drawn again through the loom reed. This part looks like a closed comb, and, it determines the setting of the number of warp yarns to the inch. The weaving operation combines the motions of the harnesses (up and down), the reed (back and forth) and the travel of the shuttle (across the width of the loom) (Reference 40).

Improved weaving techniques are being developed to reduce yarn damage and eliminate the beaming operation. Carbon yarns are woven directly from the creel through the tensioning devices, over loose rods, then through the heddles and woven as previously described.

2. CONSTRUCTIONS

Fibrous carbons and graphites are available as plain woven fabric, long shaft woven cloth, and tapes derived from these materials. Their properties vary in accordance with the fabric construction and fiber type, as shown in Table 6.

TABLE 6

TYPICAL PROPERTIES OF RAYON PRECURSOR CARBON & GRAPHITE FABRICS

TYPE	CARBON	CARBON	CARBON	GRAPHITE
FABRIC CONSTRUCTION				
WEAVE TYPE	PLAIN	5-HS	8-HS	8-HS
FILAMENTS/PLIES	720/2	960/1	720/1	720/1
THREAD COUNT, yarn/in				
WARP	27	40	45-55	48-58
FILL	23	38	45-55	45-55
PROPERTIES				
WEIGHT, oz/sq yd	6-8	8.2	7-9.5	6.5-8.5
THICKNESS, in	0.017	0.018	0.016-0.021	0.013-0.023
CARBON CONTENT, %	86-99	99	86-95	99
ASH, %	0.5-1.0	0.02-0.5	0.9	0.1
pH	7.0-10	7.0-9.5	7-9	6.5-9.5
BREAK STRENGTH, lb/in				
WARP	64	38	20-59	15-85
FILL	64	32	15-30	15-75
ELECTRICAL RESISTIVITY, ohm/sq				
WARP	0.54	0.40	0.50	0.43
FILL	0.54	0.48	0.56	0.45

The plain weave is the most common and oldest of common textile designs. It is based on an interlocking construction in which each warp pick is woven over one filling pick and under the next filling pick. This construction has uniform strength properties in the two major axes, but the high crimp leads to low strength properties and low distortion. It is a firm construction, affords fair porosity with minimum slippage, and is suitable for mascerated or chopped fabrics.

Long shaft satin fabrics have one warp end woven over several successive filling picks. The 5-harness satin cloth has one warp end woven over four and under one filling pick. It is a tighter weave and less easily distorted than 8-harness cloth. Eight-harness satin fabric has one warp end woven over seven and under one filling pick. The satin woven fabric is less open than other weaves, the most pliable construction, has the least amount of fiber crimp, conforms readily to compound curves, has balanced structural properties, and can be woven in the highest density (References 41 to 43).

Tapes are prepared by slitting 8-harness satin fabric on the bias and in the proper width. A long tape is then prepared by sewing individual pieces together with a synthetic thread. The ends of the tapes are cut on a diagonal and overlapped slightly prior to sewing.

3. COSTS

Carbon fabrics have been and continue to be relatively low cost materials. Eight-harness satin woven carbon fabric sold for $24.00 per pound in 1964. Subsequent price increases were as follows: $27.00 per pound in 1970; $30.50 per pound in 1974; $33.00 per pound in 1974, and about $37.50 per pound in 1976. The graphitized version of these same fabrics presently sells for about $42.75 per pound.

SECTION X

HIGH PURITY CARBON FABRICS

Certain defense applications require the use of very pure carbon fabrics, i.e., less than several hundred parts per million of alkali metals. These undesirable elements can be ionized at relatively low temperatures, greatly increase the electron concentration in the ablation products-air boundary layer surrounding an ablating body, and cause a significant increase in the radar cross section of the wake trailing the ablating body.

The chemical composition of carbon fibers is generally carbon, hydrogen, and oxygen. Additional nitrogen is present in PAN-based and sulfur is present in pitch-based carbon fibers. Boron and phosphorus are sometimes incorporated into the fiber before or after pyrolysis for added oxidation resistance. The ash content may run as high as 9 to 10 weight % for the boron and phosphorus containing materials. They are present in the oxide form of nonmetallic elements.

Significant levels of alkali metals are present in the original precursor fibers and yarns because special efforts have not been expended to produce a high purity fiber. Since carbon fibers are pyrolyzed at relatively low temperatures, most of the alkali metals in the precursor will remain in the carbonized fiber.

Three methods have been developed for reducing the alkali metal concentration in carbon fabrics. Halogen gases have been passed over carbon fibers at temperatures in excess of 4000°F, reacted with the sodium or other alkali metals in the fiber, formed a corresponding salt, and then removed by volatilization at the reaction temperature. Another method has been to heat carbon fibers at even higher temperatures, vaporize the contaminants, and sweep them away with a purge gas. However, these methods cause the fiber to become more crystalline, increase in density, and increase in thermal conductivity. This method is also time consuming and expensive. A third and preferred method has been developed for rayon precursor carbon fibers, which significantly lowers the alkali metal content while preserving low thermal and electrical properties, high tensile strength, and flexibility of the fibers. This method is based on ultrasonically washing the carbonized cellulosic fiber for five minutes in a

weak (1%) halogen acid (hydrobromic or hydriodic), air dry at 250°F, and then pyrolyze at 1500° to 1900°F for five minutes in an inert gas. Using this method, the alkali metal content of the fiber was reduced from about 737 parts per million (ppm) to less than 30 ppm (Reference 44).

Table 7 presents the chemical properties of regular and purified carbon fabrics. Compared to regular carbon cloths, the purified materials have a higher carbon content, lower alkali metal content, lower ash content, greater pore volume, smaller average pore size, slightly lower weight, and lower electrical resistance.

TABLE 7

CHEMICAL COMPOSITION OF CARBON FABRICS

PRECURSOR	RAYON	RAYON	RAYON	PAN	PITCH
FIBER LENGTH	CONTINUOUS	CONTINUOUS	STAPLE	CONTINUOUS	CONTINUOUS
MANUFACTURER	HITCO	HITCO	HITCO	FIBERITE	UNION CARBIDE
TRADENAME	CCA-3	CCA-3 (1641B)	CCA-28 (1641B)	T-300	VC-0139
ELEMENTAL CONTENT, %					
CARBON	95.5	96.1	99.8	92.6	96.9
HYDROGEN	-	0.11	0.11	0.5	0.9
NITROGEN	0.0	0.0	0.0	5.5	0.0
OXYGEN	-	0.04	0.05	0.2	1.3
SULFUR	0.0	0.0	0.0	0.0	0.4
ALKALI METALS, ppm					
TOTAL	737	28	40	2,248	710
SODIUM	694	8	18	2,117	660
POTASSIUM	16	6	8	20	5
CALCIUM	20	11	13	95	33
MAGNESIUM	7	3	1	15	11
LITHIUM	1	1	0	1	1
ASH, %	0.41	0.107	0.05	0.04	0.09
COSTS, $/lb	37.50	39.75	39.75	90.00	37.00

SECTION XI

ALTERNATE CARBON FABRICS

Alternate carbon fabrics are commercially available, which have similar (but not identical) properties to state-of-the-art continuous filament, rayon-based carbon materials. These carbon fabrics and their properties are given in Table 8.

1. STAPLE FIBER FABRICS

Staple rayon fibers offer the best near-term replacement for continuous filament rayon in textile carbon products. Table 9 presents typical properties of carbonized staple and continuous filament rayon. Both materials are chemically identical, but differ slightly in ash content and pH. The major differences are noted in physical features. Carbonized staple fiber has a slightly lower density, greater porosity, larger average pore sizes, and variable diameters when compared to continuous filament material.

Staple rayon fibers were obtained from three different U.S. sources and successfully processed into yarn, woven in fabric, and carbonized. A two-ply yarn of a worsted type was first prepared from 7 to 18 micron diameter rayon fibers of varying lengths, twisted ten turns per inch, then woven into the appropriate fabric construction, and finally carbonized.

When compared to continuous filament carbon fabrics, the staple carbon fabrics typically have lower breaking strengths, greater thicknesses, and slightly lower areal weights. The staple fabrics exhibit a less ordered structure and more fiber bridging between yarns. The cost of both types of carbon fabrics is the same. As the market improves for staple fabrics, it is expected that their price will be below that of continuous filament fabrics.

2. PITCH AND PAN-BASED FABRICS

Polyacrylonitrile and pitch compositions in either continuous filament or staple forms have also been processed into carbon fabrics. They offer a wide range of properties which can be altered by changing fiber chemical composition, molecular weight, and processing conditions. Both types of carbon fibers are characteristically high in fiber density, exhibit high thermal conductivity, and have high levels of alkali metals. PAN-based fabrics offer high structural properties, whereas pitch-based carbon fabrics are lower in costs.

TABLE 8

ALTERNATE 8-HS CARBON FABRICS

PRECURSOR	RAYON	PAN	PAN	PITCH	PITCH
FIBER LENGTH	STAPLE	CONTINUOUS	STAPLE	CONTINUOUS	STAPLE
MANUFACTURER	HITCO	FIBERITE	STACKPOLE	UNION CARBIDE	KREHA
TRADENAME	CCA-28 (1641)	WOVEN T-300	SWB-8	VC-0139	KCF-100 2733
FIBER PROPERTIES					
DENSITY, g/cc	1.51	1.80	1.73	1.89	1.60
CARBON CONTENT, %	96.5	92.6	97.7	96.9	99.5
ASH CONTENT, %	0.74	0.4	0.38	0.09	-
MOISTURE CONTENT, %	0.7	-	0.30	0.60	8-10
ALKALINITY, ppm	60	2,248	8,500	710	-
FABRIC PROPERTIES					
WEIGHT, oz/sq yd	8.0	11.0	9.3	13.4	13.2
THICKNESS, in	0.027	0.013	0.026	0.028	0.024
THREAD COUNT, yarns/in					
WARP	52	24	39	26	27
FILL	47	24	38	24	33
BREAK STRENGTH, psi					
WARP	15	-	39	40	-
FILL	7	-	35	40	-
COSTS, $/lb	39.75	90.0	42.50	37.00	

TABLE 9

CARBONIZED CONTINUOUS AND STAPLE RAYON FIBERS

PRECURSORS	RAYON	RAYON
FIBER LENGTH	CONTINUOUS	STAPLE
MANUFACTURER	HITCO	HITCO
TRADENAME	CCA-1 (1641)	CCA-28 (1641)
FIBER PROPERTIES		
DENSITY, gm/cc		
Tetrabromoethane	1.47	1.45
Cured Composite	1.55	1.51
Water	1.72	1.81
Benzene	1.86	1.67
POROSITY		
PERCENT	56	68
AVERAGE PORE SIZE, microns	10	20-40
TOTAL PORE VOLUME, cc/gm	1.05	1.65
DIAMETER, microns	16	7-18
CARBON CONTENT, %	96.6	96.5
ASH CONTENT, %	0.60	0.74
MOISTURE CONTENT, %	1.6	0.74
pH	8.04	8.2

SECTION XII
DEVELOPMENTAL CARBON FABRICS

While PAN and pitch-based carbon fabrics are usable in their present form for selected heatshielding applications, additional improvements in fabric uniformity and certain properties are desired. Therefore, efforts have been initiated to improve the weaveability of the yarn and produce thinner fabrics. In addition, various technical approaches are being exploited to lower the fiber density, thermal conductivity, and alkali metal concentration.

Pitch-based carbon fabrics are being developed to enhance their potential utility for heatshielding applications. A variety of developmental fabrics have been manufactured by altering the processing conditions and weaving constructions. Table 10 presents the properties of various fabrics produced to date. Progress has been demonstrated in lowering the thermal conductivity, fabric thickness, and weight of the developmental materials. However, all of the newly developed materials were lower in strength properties.

Continuous and staple PAN-based carbon fabric development is proceeding at a slow pace. Several materials have been developed and their properties are noted in Table 11. PAN-based fabrics have very high strengths and moduli, but their applications potential is limited by high fiber density, high thermal conductivity, and the presence of high alkali metal concentrations. All of these fiber property deficiencies are technically solvable. Efforts have been initiated to obtain improved materials (Reference 45).

TABLE 10

DEVELOPMENTAL PITCH-BASED CARBON FABRICS*

FIBER PROPERTIES	VC-0139	VC-0142-1	VC-0144-2	VC-0145-3
DENSITY, gm/cc	1.89	1.80	1.80	1.70
CARBON CONTENT, %	96.9	97.8	97.5	95.8
ASH CONTENT, %	0.09	0.15	0.10	0.16
ALKALINITY, ppm	710	445	590	380
SURFACE AREA, sq m/gm	0.5	1.2	1.2	1.0
YARN PROPERTIES				
THERMAL CONDUCTIVITY cal/cm-sec-°C	.040	.023	.023	.010
RESISTIVITY, ohm-cm	-	.0018	.0018	.0029
AREA, sq cm	-	.00086	.00089	.00093
PLIES	1	1	1	1
FABRIC PROPERTIES				
WEAVE	8-HS	8-HS	5-HS	PLAIN
THICKNESS, in	0.028	0.020	0.031	0.025
WEIGHT, oz/sq yd	13.4	9.6	8.9	9.2
YARN COUNT				
WARP	26	26	24	25
FILL	24	24	21	21
BREAK STRENGTH, lb/in				
WARP	40	19	15	21
FILL	40	13	45	13

*UNION CARBIDE CORPORATION PRODUCTS.

TABLE 11

DEVELOPMENTAL PAN-BASED 8-HS CARBON FABRICS

MANUFACTURER	TORAY, INC.	CELANESE	UNION CARBIDE	STACKPOLE	HITCO
TRADENAME	TORAYCA T-300	CELION HTA-7	465-H	SW-8/SHT	CCA-71 (1641B)
FIBER PROPERTIES					
LENGTH	CONTINUOUS	CONTINUOUS	CONTINUOUS	STAPLE	STAPLE
DENSITY, gm/cc	1.74	1.78	1.67	1.77	1.73
CARBON CONTENT, %	95.0	96.6	97.3	86.6	97.7
ASH CONTENT, %	0.3	0.3	0.35	1.5	0.38
ALKALINITY, ppm	2,000	510	976	7,300	100-300
FABRIC PROPERTIES					
THICKNESS, in	0.014	0.017	0.022	0.026	0.026
WEIGHT, oz/sq yd	11.0	11.0	12.5	10.0	9.3
YARN COUNT					
WARP	25	24	30	38	39
FILL	25	23	29	36	38
BREAK STRENGTH, lb/in					
WARP	-	390	90	78	96
FILL	-	355	63	34	64

SECTION XIII

CONCLUSIONS

1. Carbonaceous fibers are a specialty engineering material which are used in a variety of critical defense, aerospace, industrial, and scientific applications.

2. Carbon fibers are distinguished from graphite fibers by the heat treatment temperature employed, degree of carbon crystallinity, and relative carbon content.

3. Compared to graphite fibers, carbon fibers have a higher surface area, electrical resistivity, moisture content, wettability, elongation at break, fiber diameter, thermal expansion coefficient, and volatile content.

4. The properties of carbon fibers are controlled by the choice of raw material, heat treatment cycle, use of chemical treatments during carbonization, and application of stress during processing.

5. Carbon fibers appear to have reached a plateau for many of their properties. Future emphasis should therefore be directed to increasing production and lowering costs while maintaining desirable properties. Several potential approaches include: cheaper precursor fibers, higher production rates, and improved processes based on direct carbonization, rapid oxidation, and fast catalytic graphitization of precursor fibers.

6. Continuous filament rayon is the most commonly used precursor for fibrous carbon products.

7. Rayon yarn is a low cost material. Continuous filament rayon yarn in 1650 denier, 720 filament material sells for about $1.63 per pound and $3.63 per pound in 8-harness woven fabric.

8. Production of continuous filament rayon is decreasing in the United States. Production levels have fallen to about 78 million pounds per year, with less than two million pounds per year being used by the aerospace industry.

9. Requalification of continuous filament rayon for aerospace fibrous carbons is a costly and time consuming problem. For example, requalification of a missile heatshield containing a replacement carbon fabric costs about $20,000,000.00

10. Aerospace and military requirements for continuous filament rayon yarn are difficult to forecast with any degree of certainty, highly cyclic, and vary with the type of application.

11. There is presently a single qualified manufacturing source for aerospace continuous filament rayon yarn.

12. Continuous filament rayon is a prime candidate for future materials shortages because of low demand, highly cyclic requirements, low profitability, increased regulatory regulations, single qualified source, few substitute materials, and other factors. Continued availability of continuous filament rayon is questionable. For that reason, substitute materials are being evaluated and new materials are being developed with the desired balance of properties.

13. Various approaches have been developed for minimizing or alleviating rayon fiber shortages. The development of alternate materials represents the most feasible long-term approach because it provides minimum influence on the free enterprise system. Stockpiling rayon yarn in appropriate deniers and filament count is the best near-term, minimum risk option to ensure continued availability of fibrous carbons and graphites. These organic yarns have been stored up to six years without special environmental conditions and then converted in fibrous carbonaceous products. Storage of large quantities of rayon in a single facility is the greatest risk factor associated with materials stockpiling.

14. The leading alternate precursor fibers for fibrous carbons are staple rayon fibers, polyacrylonitrile fibers in continuous and staple forms, and pitch fibers in continuous filament form.

15. For the manufacture of fibrous carbons, staple rayon fibers offer the best near-term replacement for continuous filament rayon.

16. Staple rayon fiber is widely used for commercial products. Staple rayon fiber production will stabilize and grow at about two percent per year. Continued availability of domestically produced staple fiber is assured because of multiple commercial markets, price stability, and other factors.

17. Pitch is an attractive precursor for carbon fibers. It is readily available, very low in cost, processible into carbonized products, and has a high carbon content.

18. Polyacrylonitrile fibers also offer promise for carbon fibers. They have high carbon contents, moderate costs, available in various filament count yarns and tows, stable commercial market, and multiple sources.

19. Continuous and staple filament carbon yarns have been manufactured from various organic fiber precursors, and in the form for sewing, weaving, knitting, braiding, and filament winding.

20. Carbon fabrics represent the largest usage of fibrous carbons. They have been produced in plain, 5-harness, and 8-harness woven fabrics.

21. High strength carbon fabrics are produced by weaving high strength carbon yarns.

22. Carbon fabrics are low cost engineering materials. Regular carbon fabrics sell for about $37.50 per pound and purified carbon fabrics costs about $39.75 per pound.

23. Missile heatshielding composites require the use of very pure carbon fabrics. Commercial precursor yarns typically contain high levels of alkali metals which are largely retained in the pyrolyzed products from these materials. A satisfactory purification process has been developed for continuous filament and staple fiber rayon. Carbon fabrics based on purified rayon fabric are available with alkali metal contents about 40 parts per million. Additional efforts are required to reach acceptable contamination levels with PAN and pitch-based precursors. For the latter materials, commercial process equipment and chemicals should be adjusted to form specialty pure fibers. An alternate solution would be the development of a purification process for the standard commercial material.

24. Carbon fabrics derived from pitch and PAN-based cloths are typically high in fiber density, moderate to high alkali metal contents, and high in thermal conductivity. Fiber property changes and fabric design efforts are underway to correct these deficiencies.

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